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Catalytic Properties of Titanium Silicalites

IV. Vapour Phase Beckmann Rearrangement of Cyclohexanone Oxime

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The transformation of cyclohexanone oxime into caprolactam has been studied over the titnaium silicalite TS-1 and the related MFI analogs, ZSM-5 and Silicalite-1. The incorporation of Ti increases the yield of caprolactam, besides lowering the deactivation rate. Both oxime conversion and selectivity for the lactam increase with increasing Ti content in the zeolite. The influence of temperature and feed rate (WHSV) on the yield of caprolactam over TS-1 has been investigated at different times on stream.

INTRODUCTION

ε-Caprolactam is a valuable starting material for the manufacture of nylon fibers. The most important industrial route for the manufacture of caprolactam is the concentrated sulfuric-acid-catalyzed Beckmann rearrangement of cyclohexanone oxime (*1*). This classical method suffers from a number of disadvantages like the formation of low-value by-products like ammonium sulfate, safety hazards, corrosion, and environmental problems associated with the use of fuming sulfuric acid. To overcome these problems, attempts have been made to use solid catalysts like alumina (*2*), heteropoly acids (*3*), silica–alumina (*4*), and zeolites like Y (*5*), ZSM-5, and mordenite (*6*). However, these heterogeneous catalysts have been found to have low selectivities for lactam and deactivate rapidly. Recently, Sato *et al.* (*7, 8*) have reported that Silicalite-1 (Si/Al >3000) exhibited high activity and selectivity for lactam. It has been suggested (*8, 9*) that the active sites for this Beckmann rearrangement are the weak or neutral, isolated surface silanol groups. Modification of the surface silanol groups with trimethylchlorosilane by CVD treatment improves the catalytic performance (*9*).

Silicalite-1 (*10*) and titanium silicalite, TS-1 (*11*) belong to the MFI type of zeolites. Silicalite-1 is an all-silica molecular sieve, while titanium silicalite (TS-1) contains Ti^{4+} ions in lattice positions. In this paper, we report the use of TS-1 in the vapour-phase rearrangement (Beckmann) of cyclohexanone oxime. The details of this process over TS-1 zeolites have not, so far, been reported.

EXPERIMENTAL

Silicalite-1 and TS-1 were synthesized as per published procedures (*10–12*). A general procedure for their preparation is given below: tetraethylorthosilicate (TEOS) was mixed with the appropriate amount (almost one-half of the stoichiometrically required quantity) of aqueous tetrapropyl ammonium hydroxide (20% aq. TPA-OH solution, Aldrich) to partly hydrolyze the TEOS. To this resultant liquid mixture, a solution of the required quantity of titanium tetrabutoxide, $Ti(OBu)_4$, in dry isopropyl alcohol was added dropwise under vigorous stirring. The clear liquid was stirred for about 1 h in order to complete the hydrolysis of TEOS and $Ti(OBu)_4$. Finally, the solution of remaining TPA-OH in doubly distilled water was added slowly to the above mixture. This

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final mixture was stirred at 348–353 K for about 3–6 h to remove the alcohol. Crystallization was done statically at 443 K for 1–2 days. The crystalline product thus obtained was filtered, washed with distilled water, dried, and calcined at 823 K in air for 10 h. For a typical synthesis of TS-1 (Si/Ti = 33), the quantities of the reagents used were: TEOS = 45 g; TPA-OH (20% aq. solution) = 70 g; $Ti(OBu)_4$ = 2.2 g in 10 g isopropyl alcohol, and water = 70 g. Silicalite-1 used in the present study was also synthesized under identical conditions except that the Ti-source was not added. ZSM-5 samples were prepared from solutions containing tetrapropyl ammonium ions according to procedures reported earlier (*13*). The characterization of the samples was carried out using XRD (Philips, PW-1710 Cu$K\alpha$) and framework IR spectroscopy (Perkin–Elmer 221) (*12*a).

Cyclohexanone oxime was prepared from pure cyclohexanone by reaction with hydroxylamine hydrochloride following established procedures (*14*). The purity of the material was established to be greater than 99% by capillary gas chromatography.

The catalytic experiments were carried out in a vertical down-flow glass reactor. The zeolite powder was compacted and crushed into particles of about 1 mm diameter. About 2 g of the catalyst was used in each run. The catalyst bed was approximately 4 cm in height. A short ($\simeq$10 cm) preheating bed of α-alumina was kept above the catalyst bed. Blank experiments carried out at different temperatures in the absence of catalysts revealed very small conversions (<5%) of the oxime. The feed cyclohexanone oxime was dissolved in benzene (6 to 10 wt% solution) and injected with a syringe pump (Sage Instruments, U.S.A.) along with N_2 as a carrier gas. The reactions were carried out at atmospheric pressure at different temperatures and space velocities. During the early stages of the runs, the outlet gas was analyzed every 30 min. In the case of ZSM-5 alone, small amounts (1–2 vol%) of cracked hydrocarbons ($<C_5$) were found in the gaseous fraction in the beginning. However, after a TOS of 2 h, these could not be detected in the gas. Hence, no further gas analysis was carried out. The liquid product was collected (after cooling at 4°C) for short periods (30 min) and analyzed. Based on the weight of feed injected and the weights of products collected, the recovery was always >90 wt%. No detailed carbon balances were done. The products were analyzed in a gas chromatograph (column: capillary, HP1; cross-linked methyl silicon gum, 50 m × 0.5 mm; FID detector; carrier gas: He; G.C. model: Hewlett Packard 5880A).

RESULTS AND DISCUSSION

The major product of the reaction of cyclohexanone oxime on the different catalysts (Table 1) was found to be caprolactam. But, by-products like cyclohexanone, cyclohexenone, cyanopentane, and cyanopentene were also formed. Small amounts of high boiling condensation products were also present in the product.

It is observed that oxime conversion is found to increase with decreasing alumina content of the sample. The conversions on ZSM-5(90), ZSM-5(300), and Silicalite-1 are, respectively, 69.6, 90.9, and 95.2 wt%. The incorporation of Ti in the silicalite increases the activity further to 100%. It is noted that the by-product formation is more in the case of the aluminum-containing samples, their formation increasing with increasing Al content of the sample. As a result, the selectivity for caprolactam decreases with increasing aluminum content. The caprolactam selectivities (S_{lact}) are found to be 70.3, 71.1, and 81.6 wt% for ZSM-5(90), ZSM-5(300), and Silicalite-1, respectively. The different catalysts can be arranged in the order of decreasing lactam yields as follows: TS-1 > Silicalite-1 > ZSM-5(300) > ZSM-5(90). The incorporation of Ti in Silicalite-1 increases the selectivity further to 91.5. It appears, therefore, that the presence of Al in the zeolite is detrimental to the catalyst. It is likely that the

TABLE 1

Conversion of Cyclohexanone Oxime to Caprolactam over Different Zeolites

	Catalyst			
	ZSM-5 (90)	ZSM-5 (300)	Silicalite-1	TS-1
Si/Al	90	300	>3000	>3000
Si/Ti	—	—	—	27
Oxime conv. (%)	69.6	90.9	95.2	100
$S_{\mathrm{lact.}}$ (%)[a]	70.3	71.1	81.6	91.5
	Product distribution, (wt%)			
Cyclohexanone oxime	30.4	9.1	4.8	—
Caprolactam	48.9	64.6	77.7	91.5
Cylcohexanone	8.6	17.8	17.0	3.2
Others[b]	12.1	8.5	10.4	5.3
Caprolactam yield (wt%)[c]	34.0	58.7	74.0	91.5

Note. Reaction conditions: catalyst = 2 g; feed: 6 wt% solution in benzene; temperature = 613 K; WHSV = 3.5 h^{-1}; carrier gas: N_2 (5 ml/min); pressure = 1 atm; TOS = 5 h.

[a] S_{lact} (%) = (caprolactam in product/cylohexanone oxime conversion) × 100.

[b] Cyclohexenone, cyanopentane, cyanopentene, and higher boiling products.

[c] Yield = S_{lact} × %conversion/100.

acid sites generated by the Al^{3+} ions are responsible for the formation of the byproducts. A similar observation has also been made by Sato *et al.* (*7*). A mixture of γ-alumina + Silicalite-1 also deactivated rapidly. In fact, negligible amounts of the lactam was produced. A similar behaviour was also noticed over Fe-ZSM-5 and Fe_2O_3 + Silicalite-1.

The increased activity and selectivity due to Ti incorporation is probably due to the creation of more catalytically active centres by Ti. This is confirmed by experiments carried out over TS-1 samples containing different amounts of Ti. The results are presented in Fig. 1. As the Ti content increases both the activity for the conversion of the oxime and the selectivity for lactam formation increase.

The influences of temperature and time on stream on conversion and selectivity in the case of TS-1 and Silicalite-1 are presented in Fig. 2. The following observations can be made from the above results:

(1) Increasing the temperature of the reaction increases the conversion of oxime in the case of both silicalite and TS-1.

(2) At any temperature TS-1 is more active than silicalite.

(3) Increasing the temperature (in the temperature range 513–613 K) also increases the selectivity for lactam production in the case of both catalysts.

(4) At all temperatures (513–613 K) both

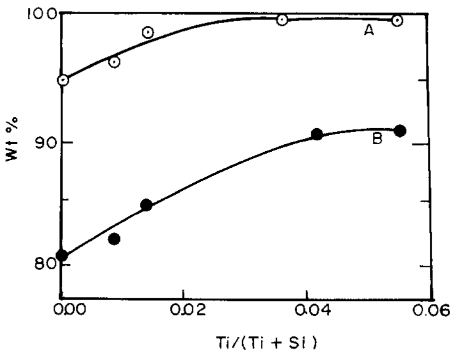

FIG. 1. Influence of titanium content of TS-1 in the conversion of oxime and selectivity for lactam: (A) oxime conversion; (B) caprolactam selectivity. Reaction conditions: catalyst = 2 g; WHSV = 3.5 h^{-1}; Temperature = 613 K; feed = 6 wt% oxime in benzene; nitrogen flow rate 5 ml/min; pressure = 1 atm; data collected at TOS = 5 h.

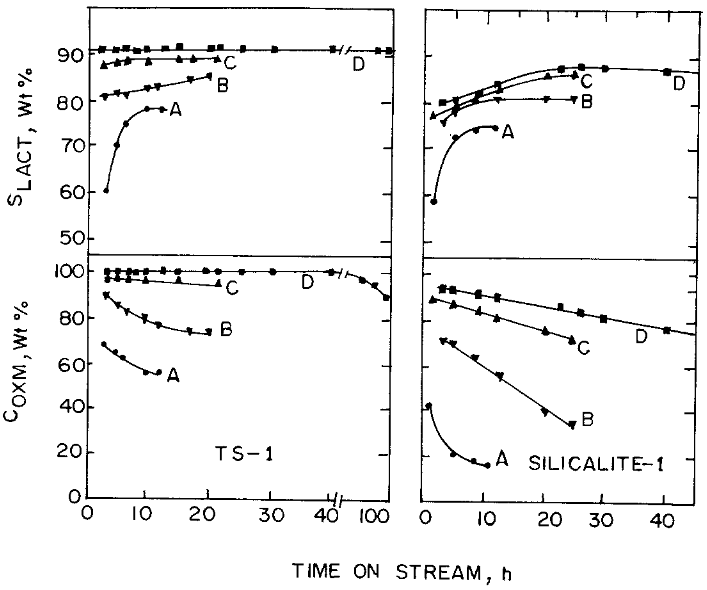

FIG. 2. Influence of temperture and duration of run on cyclohexanone oxime conversion and selectivity for caprolactam. Reaction conditions: catalyst = 2 g; temperature = (A) 513 K; (B) 543 K; (C) 574 K, and (D) 613 K. WHSV = 3.5 h^{-1}; pressure = 1 atm; nitrogen flow = 5 ml/min; feed = 6 wt% oxime in benzene.

the catalysts deactivate with time (oxime conversion decreases), the decrease in activity being more rapid in the case of Silicalite-1.

(5) The selectivity for lactam increases at all temperatures with duration of run.

(6) Despite the increasing selectivity, there is a loss in yield of lactam with duration of run, the decrease being smaller in the case of the titanium zeolite (see Table 2).

(7) The rate of deactivation decreases with increasing temperature for both catalysts.

TABLE 2

Yield (wt%) of Lactam at Different Times on Stream (cf. Fig. 2)

TOS (h)	TS-1		Silicalite-1	
	4	20	4	20
Temp. (K)				
543	71.3	61.3	52.5	25.6
574	83.7	80.9	68.6	61.2
613	92.2	91.1	74.4	72.2

The above observations suggest that the reaction is catalyzed by active centres related to both Si and Ti, and Ti-based species being more active and less prone to deactivation.

The results of the studies on the influence of feed rate variations carried out over TS-1 and Silicalite-1 are presented in Table 3. Though the % yields decrease with increasing space velocity, the actual production (% yield × space velocity) increases. But then, there is much more rapid deactivation (yield loss) at higher space velocities.

CONCLUSIONS

TS-1 is found to be the better catalyst for the transformation of cyclohexanone oxime into ε-caprolactam than the other MFI-zeolites, viz., ZSM-5 and Silicalite-1. Both conversion of oxime and selectivity for lactam production are higher over TS-1 than over the others. The deactivation rates are also smaller. Also, the yield of caprolactam increases with increase in Ti content in TS-1. In the range of temperatures (513–613 K)

TABLE 3

The Influence of WHSV on Yield of Caprolactam over TS-1 (Si/Ti = 23) and Silicalite-1 (Si/Al = 3100)

TOS (h)	TS-1 (yield wt%)			Silicalite-1 (yield wt%)		
	3	8	12	3	8	12
WHSV (h^{-1})						
3.5	92.0	92.0	93.0	77.9	78.1	78.2
7.0	80.2	77.4	72.2	74.8	69.7	65.7
14.0	65.6	61.5	54.0	72.2	55.2	46.3

Note. Reaction conditions: catalyst = 2 g; temperature = 613 K; feed: 6 wt% solution; N_2 = 5 ml/min.; pressure = 1 atm.

and WHSV's (3.5–14 h^{-1}) studied, higher temperatures and lower space velocities increase the yield of caprolactam.

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